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# Thermoluminescence and mechanoluminescence of Eu doped $Y_2O_3$ nanophosphors

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**Abstract**

Thermoluminescence and Mechanoluminescence phenomenon of $Y_2O_3$: Eu nanophosphor prepared by combustion method has reported.XRD; Optical absorption spectra have also studied. TL emission spectra show intense peak around 600 nm.

*Keywords:*Thermoluminescence,Mechanoluminescence,Yttrium Nitrate,Combustion Synthesis.

## 1. Introduction

In recent years, some attention has been paid to the study of radiation induced defects in laser and luminescent materials, since they affect the optical and stimulated emission properties. Like many oxide based materials rare earth doped $Y_2O_3$ has a resilience to ionized radiation[1].The wide variety of materials of dopants that can be incorporated allows the material to be tuned to emit in the blue($Tm^{+3}$), green($Er^{+3}$.$Tb^{+3}$) or red ($Eu^{+3}$) region of electromagnetic spectrum[2,3].Additionally ,the wide energy gap of the $Y_2O_3$ material system reduces the effect of optical absorption by the host.

Synthesis of rare earth doped $Y_2O_3$ based nanophosphor has been accomplished through a variety of techniques including spray pyrolysis, CVD, sol gel method, coprecipetation and so on. Among various methods combustion method has been studied extensively due to its simplicity and easiness to control the particle size of the products[4-6].The success of this process is due to intimate blending among the constituents using suitable fuel or complexing agent(e.g. citric acid and urea etc) in an aqueous medium followed by exothermic redox reaction between fuel and an oxidizer(i.e. nitrates)[7].The advantage of combustion method are (1) simple process: all the reactions take only few minutes, unlike the other methods that require tedious process.(2) Simple equipment-complicated method are not needed in this method.

$Y_2O_3$:Eu has attracted much attention because of its high brightness as a red color phosphor under UV or cathode ray excitation ,acceptable atmospheric stability and reduced degradation under applied voltages[8-10]. $Y_2O_3$: $Eu^{+3}$ were found to be suitable for field emission display (FED), Vacuum fluorescent display panel (PDP) devices. It has also been reported to show high photo and cathodoluminescence efficiency for $Y_2O_3$: $Eu^{+3}$.Apart from these

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properties, other characteristics of lanthanide doped oxide also play an important role in using these materials in technology. Thermoluminescence is the emission of light from sample when it is heated due to previous absorption of energy from irradiation. Yeh et al [11] have reported the UV induced thermoluminescence in rare earth doped oxide Phosphor and its possible use in UV dosimetry and they found that Eu doped $Y_2O_3$ is sensitive enough to measure background UV radiation such as sun light, bulb light etc. Mechanoluminescence is a type of luminescence induced by mechanical action on solid. We have already studied thermoluminescence and mechanoluminescence of rare earth doped $CaF_2$ crystals [12]. In this article, we have addressed the TL phenomenon and ML phenomenon of Eu doped $Y_2O_3$ prepared by combustion method.

## 2. Experimental Details

In this study Europium oxide (99.99%), Yttrium nitrate (99.99%), nitric acid, urea (90%) were used as starting raw material. To prepare $Y_2O_3$: $Eu^{+3}$ , $RE(NO_3)_3$ stock solutions was prepared by dissolving $Eu_2O_3$ in nitric acid .These two solution of $Y(NO_3)_3$ and $Eu(NO_3)_3$ were mixed according to the formula $(Y_{.95}Eu_{.05})_2O_3$ in a beaker and then a suitable amount of urea was added. A urea to metal nitrate was employed to prepare the precursor solution. Finally this sample was transferred to crucible and fired in a furnace at $600^0$C.The Synthesis reaction is

$$(2\text{-}2x)\ Y(NO_3)_3 + 2x\ RE(NO_3)_3 + 5NH_2CONH_2 \rightarrow (Y_{1-x}Eu_x)_2O_3 + 5CO_2 + 8N_2 + 10H_2O$$

The morphologies and sizes of the Eu doped $Y_2O_3$ were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 A$^o$).XRD data were collected over the range 20$^o$-80$^o$ at room temperature. The X-ray diffraction patterns have been obtained from X-ray Powder diffractometer .The particle size was determined using the sherrer's formula. The Shimatzo 1700 UV-VIS spectrometer is used to obtain the optical absorption spectra of Eu doped $Y_2O_3$ having solid sample holder .The optical absorption have been made by transmission method. For recording TL, samples were exposed to UV radiations at different time. TL glow curves were recorded with the help of TLD reader (Model 1009I).TL spectra were recorded by using interference filters. The ML was recorded by dropping a load of different mass from different heights by a homemade setup [13]. This ML peak occurred due to impulsive deformation by dropping.

## 3. Results and Discussions

### 3.1 *Structural characterization*

The XRD patterns for both samples pure $Y_2O_3$ and Eu doped $Y_2O_3$ fired at 600$^o$C are shown in Fig. 1a and fig 1b respectively. Four different peaks are obtained at 2Θ values of 29.12$^0$ , 33.78 $^o$, 48.46$^o$ and 57.56 $^o$ and the peaks correspond to diffraction at (222),(400) , (440) and (622) planes, respectively .All diffraction patterns are in good agreement with JCPDS No-41-1105 reference, proving all powders to be pure cubic $Y_2O_3$ phase having Ia3 lattice symmetry. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [14]:

$$D = 0.89\lambda/B\cos\theta$$

Where λ is the wavelength of the X-ray, θ is the diffraction pattern angle and B is the corrected full width at half maximum (FWHM) of the XRD peaks (corresponding to 2θ).

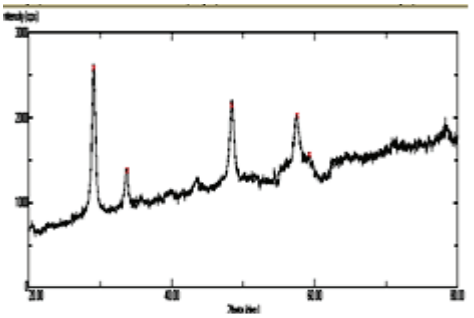

Fig 1a: XRD of pure $Y_2O_3$

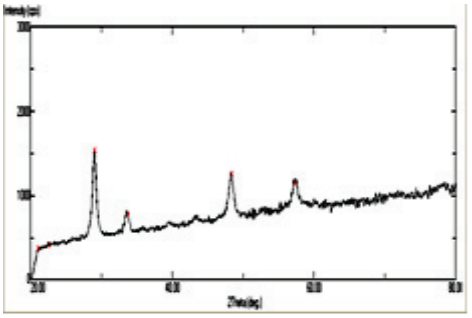

Fig 1b: XRD of $Y_2O_3$: Eu

XRD techniques indicate that the Eu doped $Y_2O_3$ was composed of nano-sized crystallites with a mean size of 14 nm.

### 3.2 *Optical Absorption*

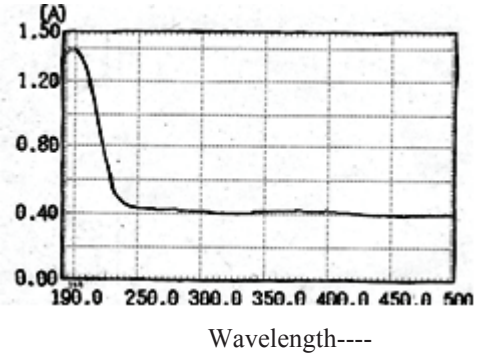


Fig 2a: Optical absorption curve of pure $Y_2O_3$

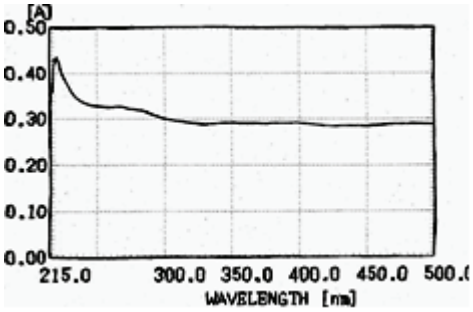


Fig 2b: Optical absorption curve of Eu doped $Y_2O_3$

Figure (2a &2b) shows the optical absorption spectra of pure and Eu doped $Y_2O_3$ in the range of 215 nm-500 nm. Optical absorption edge was obtained at 235 nm for pure $Y_2O_3$ and at 237 nm for Eu doped $Y_2O_3$. The band gap energy of the samples corresponding to the absorption edge is found 5.28eV for pure $Y_2O_3$ and 5.23 eV for Eu doped $Y_2O_3$.

### 3.3 *Thermoluminescence process*

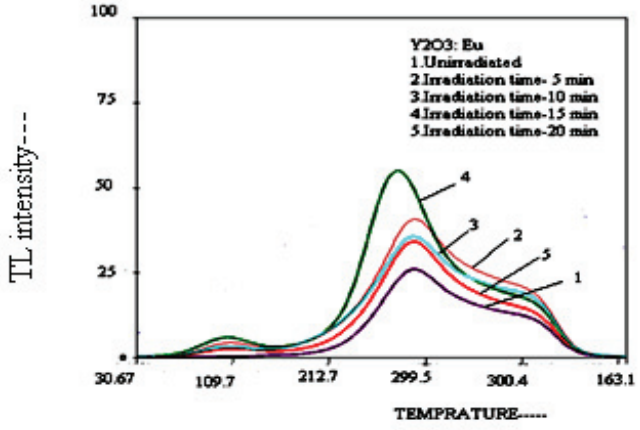

Fig 3: Variation in the TL intensity for$Y_2O_3$: Eu (5mol %) as a function of UV exposure time

Fig.3 shows the TL response curve for $Y_2O_3$: Eu (5mol %) nanoparticles for different UV exposure time at a heating rate 3$^oC$ . It is seen that at particular irradiation time 15 min high intensity of glow peak was found. In case of UV irradiated phosphors the TL response mainly generates from the surface traps, since these radiations cannot penetrate deeper and hence will not induce lattice defects. Therefore, Fig. 3 is caused by the trapped carriers which are produced during the sample processing. The TL intensity increases up to 15 min of UV exposure and afterwards it decreases.

### 3.3.1 *IR method*:

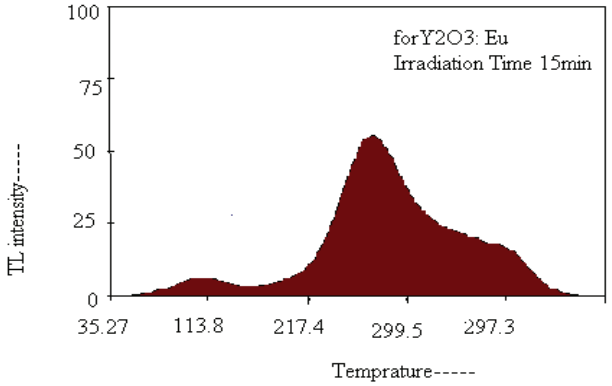


Fig 4: maximum TL peak of $Y_2O_3$: Eu for 15 min UV exposure time

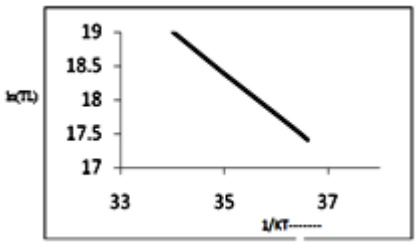


Fig5a: Activation energy for I$^{st}$ peak

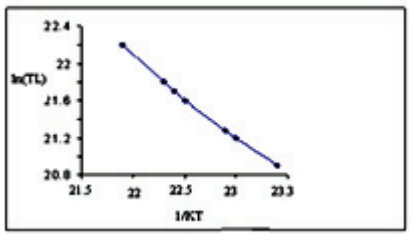


Fig5b**:** Activation energy for II$^{nd}$ peak

**Fig** 5: ln(TL) versus 1/KT graph to determine activation energy for maximum TL peak

Fig 5a, 5b show graphs of ln (TL) Vs 1/KT for I$^{st}$ and II$^{nd}$ maximum peak of fig 4 respectively. In applying initial rise method, a straight line is obtained .From the slope of line, activation energy E is evaluated for $Y_2O_3$: Eu nanophosphor of 15 min irradiation time. The activation energy of Eu doped $Y_2O_3$ is found 0.47 eV for I$^{st}$ maximum peak & 0.74 eV for II$^{nd}$ maximum peak.

### 3.3.2 *Chen's empirical method*:

The order of kinetics and the activation energy of glow curve with irradiation time 15 min was found using Chen's empirical formulae [15]. Theoretically the form factor $\mu_g$ is found using formula

$\mu_g = (T_2-T_m)/ (T_2-T_1)$.

Where, $T_m$ is the peak temperature at the maximum and $T_1$ and $T_2$ are respectively, the temperatures on either side of $T_m$, corresponding to half intensity. The trap depth or the thermal energy needed to free the trapped electrons can be calculated using the following equation

$$E_\alpha = c_\alpha (kT_m^2/\alpha) - b_\alpha (2kT_m)$$

$\alpha = \tau, \delta, \omega,$

$\tau = T_m - T_1$ is the half width at the low temperature side of the peak

$\delta = T_2 - T_m$ is the half width toward the fall-off side of the glow peak

$\omega = T_2 - T_1$ is the total half-width

$\mu = \delta/\omega$ is so called geometrical shape or symmetry factor

$c_\tau = 1.51 + 3.0 (\mu_g - 0.42)$, $c_\delta = 0.976 + 7.3 (\mu_g - 0.42)$

$c_\omega = 2.52 + 10.2 (\mu_g - 0.42)$,

$b_\tau = 1.58 + 4.2(\mu_g - 0.42)$, $b_\delta = 0$, $b_\omega = 1$

Using the value of $T_m$, $T_1$ and $T_2$ from the experimentally obtained maximum TL glow curve in Fig.4 the form factor of $Y_2O_3$ :Eu (5 mol%) is found 0.50 for the I$^{st}$ peak & 0.44 for the 2$^{nd}$ peak ,which shows first order kinetics in it.

The frequency factor [16] was calculated from equation

$$\beta E / kT_m^2 = s \exp\{-E/kT_m\}[1+(b-1)T_m]$$

Where

$\beta$ = Heating rate

E = The activation energy or trap depth (eV)

k = Boltzmann's constant ($eVK^{-1}$)

T = The absolute temperature (K)

The calculated trap parameters have been summarized in table 1.

Table 1. Trapping parameters of $Y_2O_3$: Eu nanocrystalline samples for 15 min UV irradiation at room temperature

| $Y_2O_3$: Eu | $T_m$ | Order Of Kinetics ($\mu_g$) | Activation energy(ev) | | | | Frequency(S) |
|---|---|---|---|---|---|---|---|
| (5 mol %) | | | $E_\delta$ | $E_\tau$ | $E_\omega$ | $E_{av}$ | |
| FOR I$^{ST}$ PEAK | 381.6K | 1(.50) | .52 | .43 | .48 | .47 | .38 X $10^8$ |
| FOR 2$^{ND}$ PEAK | 555.22 K | 1(.44) | .74 | .73 | .73 | .73 | .40 X $10^8$ |

From the above results, it is seen that the first trap is 0.47 eV below conduction band and the second trap is 0.73 eV below the conduction band .The intensity of first peak is less than the intensity of second peak. Therefore we can say that the concentration of first trap is less than the concentration of second trap. Since the frequency factor (s) is also called attempt to escape frequency and it is directly proportional to absolute temperature so for higher temperature glow peak frequency factor is high.

### 3.3.3 *TL emission Spectra*

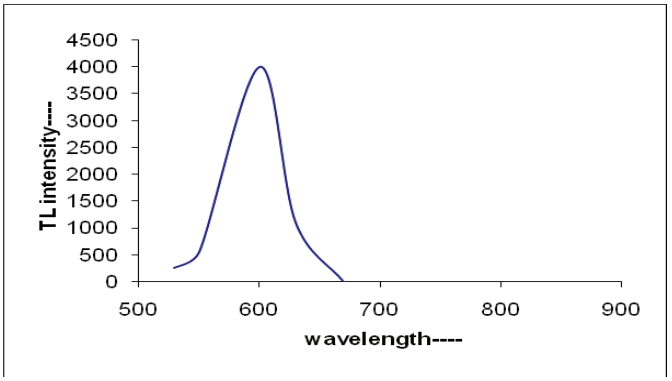


Fig 6: Thermoluminescence spectra of UV irradiated Eu doped $Y_2O_3$

Fig 6 shows the Thermoluminescence emission spectra of UV irradiated $Y_2O_3$: Eu. For prior irradiation 254 nm of UV light is used. Around 600 nm a very intense peak was observed which shows $Eu^{+3}$ Emission.

### *3.4 Mechanoluminescence process*

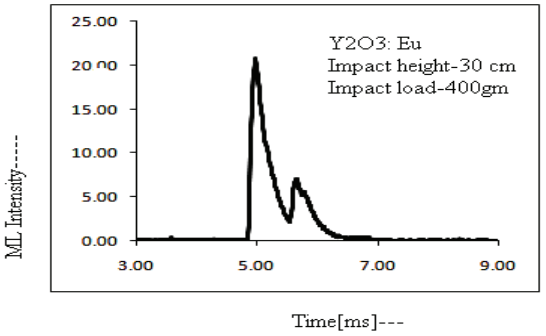


Fig 7: Mechanoluminescence of UV irradiated $Y_2O_3$: Eu phosphor from 30 cm impact height

Fig. 7 shows that when a load is dropping on rare earth doped $Y_2O_3$, then initially the ML intensity increases with time, attains a peak value and later on it decreases with time. $Y^{+3}$ ions in the unit cell occupy 24 sites with point symmetry C2 and eight sites with S6.For $Y_2O_3$: Eu, $Eu^{+3}$ have been found to preferentially occupy the C2 sites because of its non-centrosymmetric character. Therefore, $Y_2O_3$: Eu crystals are non-centrosymmetric.hence the piezoelectrification caused by fracture deformation may give rise to the light emission.

## 4. Conclusions

The preparation of $Y_2O_3$ nanophosphor (of size 10-20 nm) using a combustion method appears to be more feasible method for production. The TL properties of Eu doped $Y_2O_3$ nanophophor has been investigated for UV irradiation and it is seen that at a particular irradiation time 15 min high intensity of glow peak was found. The trapping parameters were calculated. The phosphor $Y_2O_3$: Eu is found to have first order kinetic in TL emission suggesting large electron hole recombination. TL spectra show intense peak around 600 nm which shows $Eu^{+3}$ emission. From optical absorption edge, the band gap energy was found to be 5.23 ev for $Y_2O_3$:Eu.A single peak of ML intensity was observed for Eu doped $Y_2O_3$. It is suggested that this ML peak occurred due to piezoelectrification.

**References**

[1]K.E.Bower, Y.A.Barbanel, Y.G.Shreter, G.W.Bohnert, Polymers, Phosphors *and voltaic for Radioisotope Micro batteries* vol.1, CRC press, Boca Raton, FL, 2002.

[2]S.Shinoya,W.M.Yen,*Phosphor Handbook 2*,vol.1,CRC Press ,Boca raton,FL,1999.

[3]D.Matsuura*, Red, green, and blue up conversion luminescence of trivalent-rare-earth ion-doped $Y_2O_3$ nanocrystals,* Appl.Phys.Lett.81 (2002)4526-4528.

[4] Yao G, Su L.B, and Xu J.*Eu: $Y_2O_3$ nanophosphor prepared by novel energy-saving solution combustion method*.J.Alloys Compd., 2008, 462(1-2):381.

[5]Luo X.X, Cao W.H, Xing M.M.*Preparation of nano $Y_2O_2S$: Eu phosphor by ethanol assisted combustion synthesis method*.J.Rare Earths, 2006, 24(1):20.

[6]Daldosso M,Sokolnicki J,Kepinski L,Legendziewicz J,Speghini A,Bettinelli M.*Prepration and optical properties of nanocrystalline $Ln_2O_3$:Eu phosphors*.J.Lumin.,2007,122-123(Sp.Iss.SI):858.

[7]Chavan S.V, Pillai K.T, Tyagi A.K.*Combustion synthesis of nanocrystalline yttrium: Tailoring of powder properties*.Mater.Sci.Eng.B, 2006, 132(3):266.

[8] Bhargava R.N.*Doped nanocrystalline materials-physics and applications*.J.Lumin. 1996, 70, 85.

[9] Bhargava R.N,Gallagher D,Welkar T.*Doped nanocrystals of semiconductors-a new class of luminescent materials*.J.Lumin,1994,61(1):275.

[10]Kang Y C,Park S B,Lenggoro I,W,Okuyama K.*preparation of nonaggregated $Y_2O_3$:Eu phosphor particle by spray pyrolysis method*.J.Mater.Res.,1999,14(6):2611.

[11]Yeh S.M, Su C.S.*UV induced Thermoluminescence in rare earth oxide doped phosphors: possible use for UV dosimetry*, 1996, 65(1-4):359-362.

[12] Nameeta Brahme, D.P. Bisen, R.S. Kher and M.S.K. Khokhar, *Mechanoluminescence and thermoluminesence in γ-irradiated rare earth doped $CaF_2$crystals*, Physics Procedia 2009, 2(2), pp431-440.

[13]Nameeta Brahme, Manju Shukla, D.P.Bisen, U.Kurrey, Anil Choubey, R.S.Kher, Manisha Singh. *Mechanoluminescence by impulsive deformation of gamma irradiated Er doped $CaF_2$ Crystals*. Journal of Luminescence 131(2011)965-969.

[14] Guinier, A. *X-ray Diffraction*, Freeman, San Francisco (1963).

[15]R.Chen, Y.Krish, *Analysis of Thermally Stimulated Processes*, Pergamon Press, New York (1981).

[16] C. Furetta, *Handbook of Thermoluminescence*, World Scientific, Singapore (2003).

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